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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]In this invention, it has a luminous layer which consists of a luminescent substance, and the seal of approval of the electric field is carried out. therefore, a conductive polymer layer is formed in the interface of the inorganic electrode and organic layer, and hole injection efficiency is made to come to improve in the electroluminescence devices which can transform seal-of-approval voltage into luminescence energy directly -- electroluminescence-devices Seki is carried out.

[0002]

[Description of the Prior Art]The electroluminescence phenomenon of organic materials was observed with the anthracene single crystal (J. Chem.Phys.38(1963)2042). Then, it came to observe the comparatively strong luminous phenomenon by using a solution electrode with sufficient injection efficiency (Phys.Rev.Lett.14(1965)226). Energetically after that conjugate organic host substance and condensation benzene ring. Research which formed the organic luminescence substance with the conjugate organic active agent which it has was done (USP3, 172 and 862, USP3, 172 and 050, USP3,710,167, J.Chem.Phys.44(1966)2902, J.Chem.Phys.50(1969)14364). However, each organic photogene mentioned here had the fault that the electric field which thickness is thick and needs it for luminescence became high.

[0003]On the other hand, research of the thin film by vacuum deposition was done, and the effect showed up in driver voltage reduction. However, it did not come to obtain the luminosity of the practical use level (Polymer 24 (1983) 748, Jpn.J.Appl.Phys.25(1986)L773).

[0004]In recent years, the element which formed the charge transport layer and the luminous layer in inter-electrode with vacuum deposition from Eastman Kodak Co. is proposed, and high-intensity [in low driver voltage] came to be realized (Appl.Phys.Lett.51(1987)913,

USP4,356,429). The research was activated further, the three-layer type element etc. which separated that of carrier transport and a luminescence group were examined, and the organic electroluminescence element went into the practical use stage (Jpn.J.Appl.Phys.27(1988) L269, L713).

[0005]

[Problem(s) to be Solved by the Invention]However, the element above-mentioned [these] is weak to exfoliation by water adsorption or thermal degradation, and by using it for a long time has shown that the increase in a dark spot becomes remarkable. Although these degradation is made into an inorganic electrode and the causes with main exfoliation by the interface of an organic layer, these problems are not yet solved fully.

[0006]Therefore, the purpose of this invention controls thermal degradation of these organic electroluminescence elements, and there is in providing the electroluminescence devices which are excellent in heat resistance and endurance.

[0007]

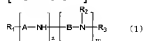
[Means for Solving the Problem]A result in which this invention persons inquired wholeheartedly to achieve the above objects, Between an inorganic electrode (ITO electrode) which is the anode, and an organic hole transporting bed, as a buffer layer. It found out that it was very effective to endurance to make into a carrier transport auxiliary layer an oligo aniline derivative expressed with the following general formula (1) which is excellent in adhesion with an inorganic electrode, and has conductivity, and to provide it one layer, and resulted in this invention.

[0008]In this case, giving conductivity, giving the performance as an electrode and maintaining hole transport capacity by doping a sulfonic acid derivative of the following general formula (4) to an oligo aniline derivative. The compatibility of an inorganic electrode and a hole transporting bed which is organic layers was raised, and it comes to control interfacial phenomena, such as exfoliation, and came to raise an element's own endurance.

[0009]That is, this invention is a general formula (1) as a carrier transport auxiliary layer between the anode and an organic layer in the anode and the negative pole, and an electrolytic luminescence element that comprises an organic compound of one layer or two or more layers ****(ed) among these.

[0010]

[Formula 4]

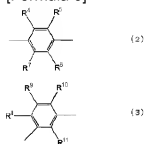


[0011](The inside of a formula, R^1 , R^2 , and R^3 show the monovalent hydrocarbon group or ORGANO oxy group of unsubstituted or substitution independently, respectively, and A and B

are a general formula (2) or a general formula (3) independently, respectively.)

[0012]

[Formula 5]



[0013]Come out, are a basis of the bivalence expressed and independently $R^4 - R^{11}$, respectively A hydrogen atom, It is a monovalent hydrocarbon group of a hydroxyl group, unsubstituted, or substitution or an ORGANO oxy group, an acyl group, or a sulfonic group, and m and n are one or more positive numbers independently, respectively, $m+n \leq 20$ is satisfied. It is related with the electrolytic luminescence element using the electrical conductivity thin film which forms a salt with the oligo aniline derivative expressed and an electronic receptiveness dopant.

[0014]

[Embodiment of the Invention]Although the method of a synthetic method in particular of the oligo aniline derivative in this invention is not limited, it is compoundable by the method described below, for example.

[0015]That is, the method of carrying out the condensation reaction of aromatic amine and the phenols by a dehydrating condensation reaction or the method to which aromatic amine and an aromatic amine hydrochloride are made to react by a molten state is common.

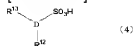
[0016]Although substituent R^1 of the oligo aniline part of a general formula (1) and $R^3 - R^{11}$ are generally hydrogen, In order to raise the solubility over a solvent, an alkyl group, an alkoxy group, a cyclohexyl group, a biphenyl group, a bicyclo hexyl group, a phenyl cyclohexyl group, etc. are suitable. For example, although there are generally a methyl group, an ethyl group, a propyl group, etc. as an alkyl group, and 1 to 4 is common as a carbon number, the introduction to the carbon number 20 is possible. Although the number of m and n of an oligo aniline part is one or more positive numbers independently, respectively, when the conductivity is taken into consideration, two or more are desirable, and when the solubility over the solvent is taken into consideration, 20 or less are desirable.

[0017]The monovalent hydrocarbon group of a hydrogen atom, a hydroxyl group, unsubstituted, or substitution or the ORGANO oxy group, the acyl group, the alkyl group of the carbon numbers 1-20, or the alkoxy group of the carbon numbers 1-20 is [substituent R^2] suitable. For example, although there are generally a methyl group, an ethyl group, a propyl

group, etc. as an alkyl group, and 1 to 4 is common as a carbon number, the introduction to the carbon number 20 is possible.

[0018]And it is a general formula (4) as acid. [the dope (salt formation) of the oligo aniline derivative of this invention and dopant which are expressed with said general formula (1) obtained by a manufacturing method which was described above]

[Formula 6]



[0019](D expresses the benzene ring, a naphthalene ring, the Atr Seng ring, a phenanthrene ring, or heterocycle, and R^{12} and R^{13} express a carboxyl group or hydroxyl independently, respectively.) -- the sulfonic acid derivative which is easy to cause the intermolecular interaction expressed is desirable. For example, a sulfosalicylic acid derivative, for example, 5-sulfosalicylic acid, and a sulfo phthalic acid derivative, for example, 4-sulfophthalic acid etc., are mentioned as such a molecule. Although it changes with molecular weights of an oligo aniline derivative as doping concentration, it is preferred to add so that it may generally become one or less dopant to one nitrogen atom in an oligo aniline derivative.

[0020]It will not be limited especially if an oligo aniline derivative is dissolved in forming the coat of an oligo aniline derivative. As an example of these solvents, N-methyl pyrrolidone, N,N-dimethylacetamide, N,N-dimethylformamide, etc. can be mentioned. These may be independent, or they may be used, mixing. If independent, even if it is a solvent [have] which a uniform solvent obtains, the solvent may be used in the range from which a uniform solvent is obtained, adding. As the example, ethylcellosolve, butyl cellosolve, ethylcarbitol, butylcarbitol, ethylcarbitol acetate, ethylene glycol, etc. are mentioned.

[0021]This solution can be applied on a substrate and an oligo aniline coat can be made to form on a substrate by evaporating a solvent. A solvent should just evaporate and 80 to 150 °C of temperature in this case is usually enough.

[0022]Although a dip method, a spin coat method, a decalcomania method, a roll coat, brush coating, etc. are mentioned as a coating method at the time of forming an oligo aniline thin film of this invention, it is not limited in particular. After isolating an oligo aniline derivative already doped by a general formula (4), it can also be made to laminate with a vacuum deposition method. As for especially the thickness, although not limited, a thing thin as much as possible is desirable, and 0.5-1000 Å is usually preferred in order to raise outward luminous efficiency.

[0023]Shape of electroluminescence devices forms first an oligo aniline thin film of the above-mentioned statement on ITO which is an inorganic electrode. What ITO generally performed washing processing of reverse sputtering, ozonization, acid treatment, etc. at this time, and removed foreign matters, such as a surface organic matter, is used. Thus, organic materials

for electroluminescence are laminated to an obtained substrate with an electrode. Although there are various forms in the present laminated structure, and not limited in particular, an element generally laminated with vacuum deposition in order of a hole transporting bed, a luminous layer, and a carrier transport layer is used.

[0024]N,N,N-tris(p-toluy)l amine (TPD) which is generally the 3rd class aromatic amine although a hole carrying material in particular is not limited, 1,1-bis[(di-4-toluy)l amine) phenyl] cyclohexane, N,N'-diphenyl-N,N'-bis(3-methylphenyl)(1,1'-biphenyl) 4,4'-diamine, N,N,N,N'-tetrakis (4-methylphenyl) (1,1'-biphenyl)-4,4'-diamine, N,N'-bis(1-naphthyl)-N,N'-diphenyl-1,1'-screw phenyl-4,4'-diamine (alpha-NPD), a 4,4',4"-tris(3-methylphenylamino) triphenylamine, etc. are mentioned. In addition, a pyrazoline derivative is used.

[0025]Although not limited especially concerning carrier transport material, generally an aromatic condensed ring system compound and a metal complex compound are used in many cases. For example, tris(8-hydroxyquinoline) aluminum (Alq), Metal complex systems, such as bis(10-hydroxybenzo [h] kino rate)beryllium (BeBq2), A 1,3,4-oxa thiazole derivative, a 1,2,4-triazole derivative, a bis(benzimidazole)derivative of perylene dicarboxyimide, a thiopyran sulfone derivative, etc. are mentioned.

[0026]As a luminescent material, Alq, tris(5-cyano 8-hydroxyquinoline) aluminum (aluminum (Q-CN)), etc. are mentioned as a metal complex system, Although an oxa thiazole system, for example, a biphenyl p-(t-butyl) phenyl-1,3,4-oxa thiazole, ** triazoles, allylenes, and coumarins are mentioned as coloring matter, it is not limited in particular.

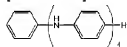
[0027]These materials are laminated by a vacuum deposition method one by one, and a MgAg alloy is vapor-deposited by the upper part as the negative pole. Thus, electroluminescence devices which show luminescence of a specified wavelength are obtained by carrying out the seal of approval of the electric field to an obtained element.

[0028]Although an example is shown below and this invention is explained to it still in detail, it is not limited to this.

[0029]

[Example]Example 1 aniline pentamer [0030]

[Formula 7]



[0031]It was made to dissolve in a DMF solvent and 5-sulfosalicylic acid was doped to it.

Doping quantity and varnish creation conditions are shown in Table 1.

[0032]

[Table 1]

Table 1 Varnish creation conditions. ----- Run No. Aniline pentamer Dopant

DMF mmol g mmol g g. ----- 1 2.2595 1.00 2.260 0.574 29.91 2 2.2595 1.00 4.519 1.148 40.81 3 2.2595 1.00 6.779 1.723 51.74 4 2.2595 1.00 9.038 2.297. The electrical property of the thin film 62.64 ----- Obtained is shown in the following table 2. [0033]

[Table 2]

Table 2 Electrical property of conductive thin film. ----- Run No. 1 2 3 4. --- -----, Mobility --- 9.19 13.7 2.61, carrier density --- 4.52×10^{12} 8.23×10^{11} 2.19×10^{10} conductivity --- 2.12×10^6 8.15×10^7 1.26×10^8 ionization potential . 5.11 5.08 5.00 The 4.94 ----- above-mentioned written varnish formed membranes with the spin coat. It calcinated after that and the conductive thin film was obtained. By vacuum evaporation, the obtained thin film was light-emitting-device-ized promptly. Element structure laminated alpha-NPD and 500A of Alq(s) on the ITO electrode, respectively, and laminated MgAg as a 2000A cathode terminal in the upper part.

[0034] Thus, luminance property was measured about the produced element. The result is shown in Table 3.

[0035]

[Table 3]

Table 3 The electroluminescence-devices characteristic. ----- Run 1 2 3 4. -----, Luminescence starting potential (V) --- 2.5 2.5. 2.5 Maximum luminance (cd/m^2) --- 16460 (11V) 17540 (11V) 13440 (11V) Current efficiency (cd/A) --- 6.40 (11V) 8.56 (11V) 7.27 (11V). The ----- example 2 aniline hexamer was dissolved in the DMF solvent, and 5-sulfosalicylic acid was doped to it. Doping quantity and varnish creation conditions are shown in Table 4.

[0036]

[Table 4]

Table 4 Varnish creation conditions. ----- Run No. Aniline hexamer Dopant DMF mmol g mol g g. ----- 11.8738 1.00 1.874 0.476 28.04 2 1.8738 1.00 3.748 1.953 37.11 3 1.8738 1.00 5.621 2.429 46.15 4 1.8738 1.00 7.495 2.905. 55.20 5 1.8738 1.00 9.3693.381 The electrical property of the thin film 64.24 ----- Obtained is shown in the following table 5.

[0037]

[Table 5]

Table 5 Electrical property of conductive thin film. ----- Run No. 1 3 5. -----, mobility 6.00 21.4 19.1 carrier densities . 1.78×10^{11} 5.10×10^{10} 1.44×10^9 conductivity 1.72×10^7 1.74×10^7 3.78×10^8 ionization potential 5.13 4.98 5.00. ----- [0038] The above-mentioned written varnish formed membranes with the spin coat. It

calculated after that and the conductive thin film was obtained. By vacuum evaporation, the obtained thin film was light-emitting-device-ized promptly. Element structure laminated alpha-NPD and 500Å of Alq(s) on the ITO electrode, respectively, and laminated MgAg as a 2000Å cathode terminal in the upper part. Thus, luminance property was measured about the produced element. A result is shown in Table 6.

[0039]

[Table 6]

Table 6 The electroluminescence-devices characteristic. ----- Run 1 3 5. -----

----- Luminescence starting potential (V) --- 2.5 2.5 Maximum luminance (cd/m^2) --- 16540 (11V) 17440 (11V) Current efficiency (cd/A) --- 5.40 (11V) 5.27 (11V). -----
 ---[0040]The luminescent characteristic was measured about element structure ITO/alpha-NPD/Alq/MgAg which does not use the auxiliary layer as comparative example 1 comparative example. Each class other than ITO was formed by the vacuum deposition method, respectively.

Run 1 luminescence starting potential (V) 2.75 maximum luminance (cd/m^2) 6000 (14.75V) current efficiency (cd/A) 5.00 (8V) [0041]The luminescent characteristic was measured about element structure ITO / auxiliary layer / alpha-NPD/Alq/MgAg which used the conductive polymer which made polyphenetidine dope camphor sulfonic acid as an auxiliary layer as comparative example 2 comparative example. The auxiliary layer was made to form with a spin coat method. Each class other than ITO was formed by the vacuum deposition method, respectively.

Run 1 luminescence starting potential (V) 2.75 maximum luminance (cd/m^2) 10300 (15.5V) current efficiency (cd/A) 5.38 (12.25V) [0042]

[Effect of the Invention]The tunic which the oligo aniline derivative used for this invention is easy to compound, and is excellent in heat resistance, tunic intensity, and coat description considering this as one of the raw materials, and has antistatic property or low charge storage nature is obtained. A reliable electrolytic luminescence element can be obtained by using such oligo aniline derivative ** as an electric charge pouring auxiliary layer of electroluminescence devices.

[Translation done.]